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Chapter 6 (Physical chemistry)

B. Electrochemistry (01)

B] Electrochemistry:

- **(6.1) Electrochemistry** is the branch of physical chemistry which deals with interconversion of electrical energy and chemical energy. Electrochemistry holds a central position in chemistry because it acts as a bridge between thermodynamics and rest of chemistry and it enables to study ionic reactions in detail.

- A substance which decomposes on passing current through it is known as *electrolyte* and phenomenon of decomposition is called *electrolysis*.

- Spontaneous oxidation-reduction (redox) reactions can be used to produce electric current under suitable conditions. The device used for this purpose is called *cells*. There are two types of cells namely electrolytic & electrochemical cells. Chemical reactions can be forced to proceed by passing electric current. A device used for this purpose is called *electrolytic cell*.

- **Conductors:** Substances which allow electric current to flow through them are called conductors while which do no permit the flow of electric current are called insulators. There are two types of conductors.

1. **Metallic conductors:** Metallic conductors are also known as electronic conductors.

   - Conduct electric current due to the mobility of free electrons in a particular direction when a potential difference is applied across the ends of a conductor.
   - The conductance of metallic conductor decreases with the rise in temperature because the residual positively charged ions starts vibrating at high temperature and collide with some of the free electrons so there is increase in resistance.

2. **Electrolytic Conductors:**

- It is also known as electrolytes are substances which give positively charged ions called cations and negatively charged ions called as anions in molten state or in aqueous solution.
- They conduct current due to movement of ions and undergo chemical decomposition of reduction of cations at cathod and oxidation of anions at anode.
- Electrolytic conductors are of two types
  a) Strong electrolyte: Which ionized completely & conduct electricity to a large extent eg HCl, HNO_3, NaOH, KOH, NaCl etc
  b) Weak Electrolyte: Which does not ionized completely & hence do not conduct electricity to a large extent eg CH_3COOH, NH_4OH etc.

(6.2) Conductance of electrolyte solutions:

The capacity of conductor to carry the electrical current (energy) is known as the conductance or conductivity. We generally come across with two conductors i.e. metallic and electrolytic conductors.

The conductance of electrolyte solution is due to migration of ions through the solution to the electrodes. The conductance (C) of an electrolyte is the reciprocal of its resistance (R). Thus,

$$C = \frac{1}{R}$$

It is measured in ohm^{-1} or mho or Siemens (S).

Resistance of any uniform conductor varies directly as its length and inversely to its area of cross section.

$$R \propto \frac{l}{a} = \rho \, . \, \frac{l}{a}$$

Where, ρ = constant called specific resistance or resistivity

l = length of conductor

a = cross sectional area of conductor

When $l = a = 1$, $R = \rho$

Hence, specific resistance is the resistance of conductor of unit length and unit cross sectional area OR It is the resistance of 1 m^3 material.

Specific conductance (k): *"The conductance of one centimeter cube (1 cm^3) or one cubic meter (1 m^3) solution of an electrolyte is known as specific conductance."* It is denoted by 'k' (Kappa).

Specific conductance (k) is reciprocal of specific resistance (ρ).

$$\therefore \quad k = \frac{1}{\rho} \quad \text{……………………(1)}$$

$$R \propto \frac{l}{a} \quad \text{…………………………..(2)}$$

$$R = \rho\frac{l}{a} \quad \text{…………………………(3)}$$

$$\rho = R.\frac{a}{l} \quad \text{………………………..(4)}$$

Substitute this value of ρ from equation 4 in equation 1

$$\text{OR} \quad k = \frac{1}{\rho}.\frac{l}{a}$$

Where, l = length of conductor

a = cross sectional area of conductor

For electrolytes specific conductance is the conductance of one meter cube of solution. Its CGS unit is $ohm^{-1}\ cm^{-1}$ or $S\ cm^{-1}$ & SI unit is $ohm^{-1}\ m^{-1}$ or $S\ m^{-1}$.

Equivalent conductance (λ_v): *It is defined as the conductance of a solution containing one Kg equivalent of electrolyte placed between two parallel electrodes 1 meter apart*. It is denoted by (λ_v).

OR

"The conductance of one gram equivalent of an electrolyte, dissolved in 'V'cc of water."

It is the product of specific conductivity and the volume of solution containing 1 kg equivalent of electrolyte.

$$\lambda_v = k\ .V$$

In general, if an electrolyte solution contains '*N*' gram equivalent in 1000 cc of solution. Then,

$$\lambda_v = \frac{k \times 1000}{N}$$

In CGS system its unit is mho cm^2 eq^{-1} or S cm^2 eq^{-1}. The SI unit of equivalent conductance is mho m^2 eq^{-1} or S m^2 eq^{-1}

Molar conductance (μ_v): *"It is defined as conductance of solution containing one mole of electrolyte placed between two parallel electrodes one meter apart."* It is denoted by (μ_v).

OR

"The conductance of the solution containing one gram mole of electrolyte is known as molar conductance".

If one gram mole of electrolyte dissolved in '*V*'cc of solution, then its molar conductance is given as

$$\mu_v = k \,.\, V$$

k = specific conductance

V = volume of solution in meter cube containing 1 gm molecular weight of electrolyte.

In CGS system its unit is mho cm^2 mol^{-1} or S cm^2 mol^{-1}. The SI unit of equivalent conductance is mho m^2 mol^{-1} or S m^2 mol^{-1}

(6.3) Comparative study of Specific conductance, Equivalent conductance and Molar conductance.

Sr. No	Specific conductance	Equivalent conductance	Molar conductance
1	*The conductance of one centimeter cube (1 cm3) or one cubic meter (1 m3) solution*	*The conductance of one gram equivalent of an electrolyte, dissolved in 'V'cc of water*	*The conductance of the solution containing one gram mole of electrolyte*
2	'*k*' (Kappa)	(λv)	(μv)
3	CGS unit is ohm^{-1} cm^{-1} or S cm^{-1}	mho cm^2 eq^{-1} or S $cm^2 eq^{-1}$	mho cm^2 mol^{-1} or S cm^2 mol^{-1}
4	SI unit is ohm^{-1} m^{-1} or S m^{-1}.	mho m^2 eq^{-1} or S m^2 eq^{-1}	mho m^2 mol^{-1} or S m^2 mol^{-1}
5	$k = \frac{1}{R} . \frac{l}{a}$	$\lambda v = k.v$	$\mu v = k.v$